Evaluating Chemical Reactivity Hazards

Presentation to:
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Center for Chemical Process Safety

CCPS

Center for Chemical Process Safety

- Since 1985
- Sponsor-driven arm of AIChE
- More than 80 Sponsors, including DOE
- More than 70 books and publications
- Find the book you need at:

http://www.aiche.org/ccps/products

CCPS Mission

To promote continuous improvement in chemical process safety we:

- Advance state-of-the-art
  - **process safety technology and management practices**
- Serve as a premier resource
  - **for information on process safety**
- Foster process safety in education
  - **chemical and other engineering and science**
- Communicate PS as key industry value

Presentation Outline

- How this project came about
- Examples of reactivity accidents
- Define reactivity hazards
- Process for addressing reactivity hazards
- Handout

Origins of This Project

- Most major chemical companies have strong reactive hazard evaluation programs
  - Many chemical plants have learned painful lessons about reactive chemicals
- No one program addresses all issues
- Regulatory agencies considering the topic
- CCPS undertook a two-prong project to:
  - Prepare a short pamphlet for distribution to smaller chemical handling enterprises
  - Create a book incorporating best practices from its sponsors

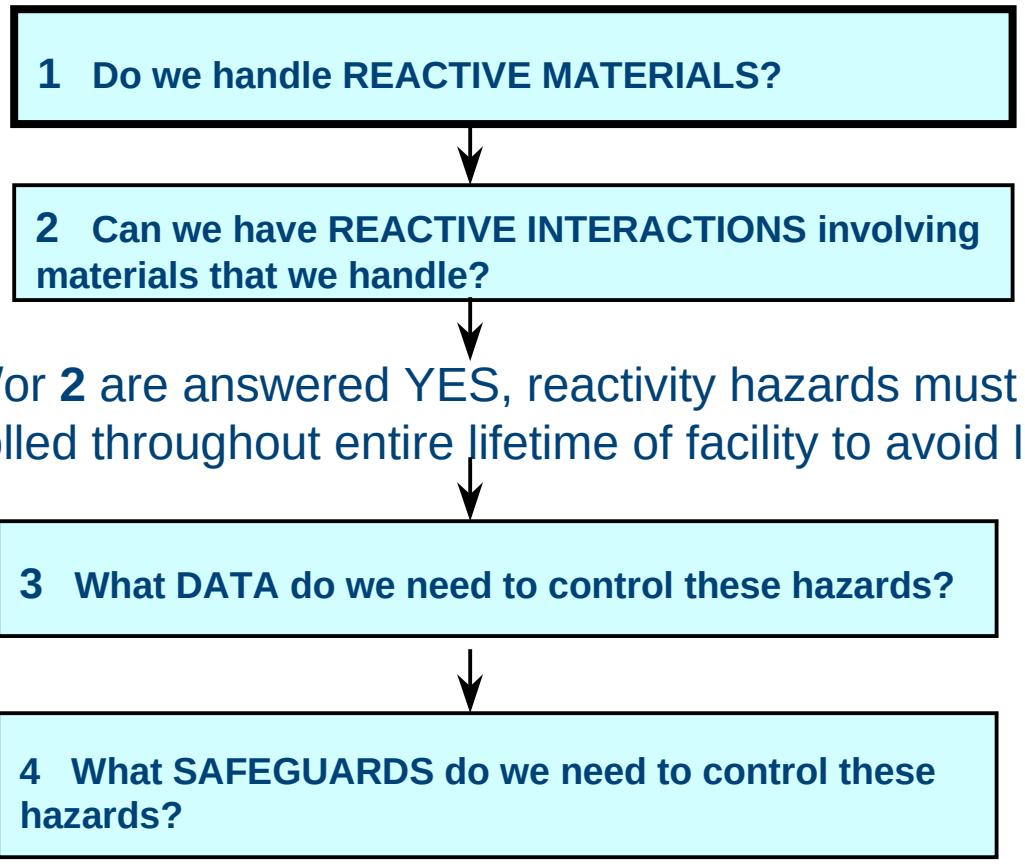
Could this happen to me?

- Rain leaked into drums of swimming pool chemicals: Explosion, fire, chlorine release, 275 injured
- Cleaning agents mixed together: toxic gas produced, 23 injured
- Insecticide stored near hot exhaust pipe: explosion, fire, 3 killed
- Water leaked from shaft seal into mixed dry powders: powders reacted and exploded, 5 killed

Do I handle reactive chemicals?

- Yes: All chemicals react
  - Must separate safe reactions that produce useful products from reactive material hazards
- Two kinds of reactive material hazards
  - A material that is unstable or self reactive
  - Two or more materials that interact unplanned

Reactivity hazard management process



If **1** and/or **2** are answered YES, reactivity hazards must be contained and controlled throughout entire lifetime of facility to avoid loss/injury incidents

Do I handle reactive materials?

- Instability: runaway reaction hazards, instability, thermal sensitivity, & incompatibility
- Can hazards, i.e. a dangerous release of
  - Blast energy
  - Heat
  - Toxic Fumes or Gases

  occur during normal or abnormal situations
- An ***Intrinsic Evaluation*** must be done

Intrinsic Evaluation

Does literature or common knowledge of material say that material is:

- Unstable
- Polymerizing
- Pyrophoric
- Peroxide Former
- Water Reactive
- Oxidizer

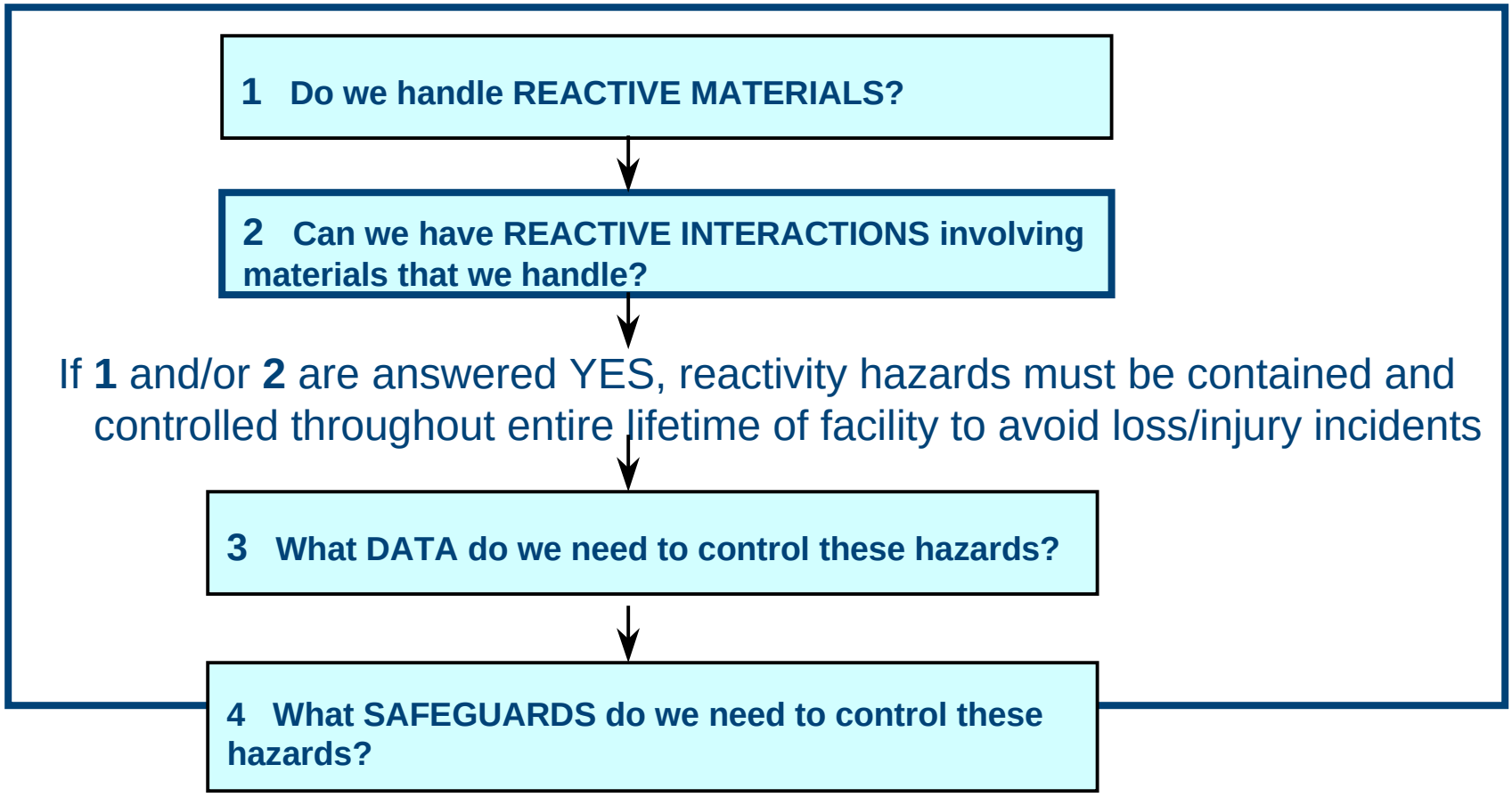
Reactivity Hazard Definitions

Reactivity Hazard	General Definition	Examples
UNSTABLE (DECOMPOSING, THERMALLY SENSITIVE, SHOCK SENSITIVE, EXPLOSIVE)	Has the tendency to break down (decompose) over time or when exposed to conditions such as heat, sunlight, shock, friction, or a catalyst, with the resulting decomposition products often being toxic or flammable. Decomposition can be rapid enough to give an explosive energy release, and can generate enough heat and gases for fires/explosions.	Trinitrotoluene (TNT), dibenzoyl peroxide, ethylene oxide, acetylene, picric acid, hydrogen peroxide (concentrated)
POLYMERIZING	Has the tendency to self-react to form larger molecules, while possibly generating enough heat/gases to burst a container	Acrylic acid, styrene, 1,3-butadiene
PYROPHORIC	Will ignite spontaneously when exposed to air	Phosphorus, silane
PEROXIDE FORMER	Has the tendency to slowly react with oxygen, such as from being exposed to air, to form unstable organic peroxides	1,3-Butadiene, isopropyl ether
WATER REACTIVE	Will react with water or moisture. Some react slowly; others violently. Heat and flammable/toxic gases may be produced.	Sodium, sulfuric acid, acetic anhydride
OXIDIZER	Will give up oxygen easily or readily oxidize other materials.	Chlorine, nitric acid

Where can I get help?

- Material Safety Data Sheets
  - See section labeled “Reactivity” or “Stability and Reactivity”
  - Look at “Firefighting” section for clues
  - Note MSDSs vary widely – obtain several and compare
- Call your vendor
- *Bretherick’s Handbook of Reactive Chemical Hazards,* www.chemweb.com

Reactivity hazard management process



Can I have reactive interactions?

- Correct materials mixed, but in wrong order or in wrong amounts
- Contaminant introduced: unintended material, rust, water, air, lubricant, etc.
- Abnormal temperature or pressure
- The key is to identify whether these interactions can occur, regardless of likelihood
- A ***Compatibility*** evaluation must be done
- A Process Hazard analysis may be required

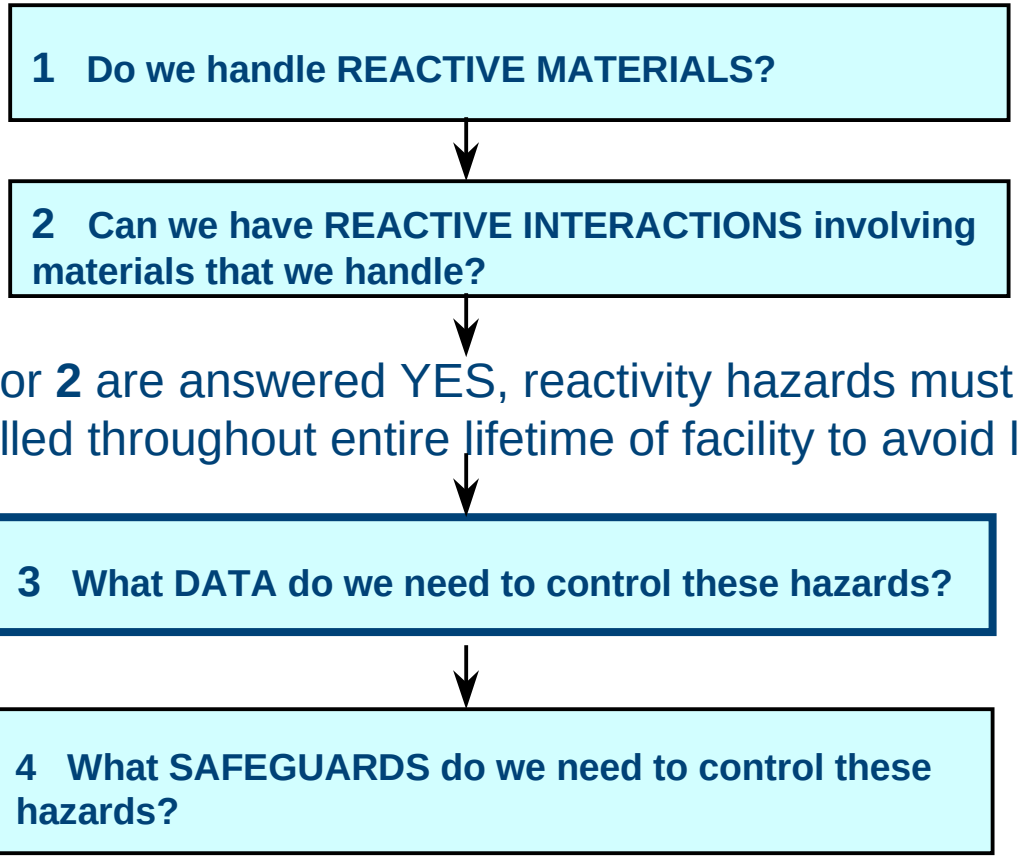
Compatibility Chart

Will these materials interact?	Acetic Acid	Acetic Anhydride	Cooling H2O	Sulfuric Acid	50% Caustic	Lube Oil	Cleaning Solution
Acetic Acid							
Acetic Anhyd.	***Yes***						
Cooling H2O	***No***	***Yes***					
98% Sulfuric Acid	***Yes***	***Yes***	***Yes***				
50% Caustic	***Yes***	***Yes***	***Yes***	***Yes***			
Lube Oil	***No***	***No***	***No***	***Yes***	***No***		
Cleaning Solution	**First, Find out what cleaning solution contains, then determine interactions**						

Compatibility Chart Resources

- Resist temptation to say, “that can’t happen”
- References (MSDS, Vendor, Bretherick)
- NOAA Chemical Reactivity Worksheet
  http://response.restoration.noaa.gov/chemaids/react.html
- Specialized testing – calorimetry
  - ARC, DSC
  - Be conservative with results
  - Scale matters

Reactivity hazard management process



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Safeguards

- Inherent safety
- Codes and standards
  - e.g. NFPA 432 for organic peroxides
- Lines of defense
  - Training, labeling, housekeeping
  - Equipment and work layout - segregation
  - Piping design
  - Instrumentation, interlocks, and alarms
  - Containment

Process Hazard Analysis

Method depends on type of hazard. Examples:

- "What-if" checklist
- HAZOP
- Layers of Protection Analysis
- For assistance
  - CCPS Books
  - Consultants

References

- Lewis, *Sax's Dangerous Properties of Industrial Materials*, ISBN 0471354066
- NFPA 49: *Hazardous Chemicals Data*, www.nfpa.org
- U.S. Dept. of Transportation. *Emergency Response Guidebook*, http://hazmat.dot.gov

✓ *Guidelines for Chemical Reactivity Evaluation and Application to Process Design*

- Yoshida, Wada and Foster, *Safety of Reactive Chemicals and Pyrotechnics*, ISBN 0444886567

✓ Lees, *Loss Prevention in the Process Industries*

✓ *Guidelines for Safe Storage and Handling of Reactive Materials*

✓ *Guidelines for Process Safety in Batch Reaction Systems*

✓ *Guidelines for Hazard Evaluation Procedures, Second Edition with Worked Examples*

✓ = Available from CCPS

When Do I Perform This Evaluation?

- As you select a manufacturing or processing operation for the first time
- If there is a change in materials processed or processing conditions beyond the norm
- If you have never performed the evaluation in your facility before

Select Murphy's Laws

- If anything can go wrong, it will
  - And at the worst possible time
- If anything **can't** go wrong, it will
- If something that should have gone wrong went right the last time, that doesn't mean it won't go wrong the next time